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STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION

OF THE ALKALINE SILVER ELECTRODE

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A B S T R A C T

A reproducible roughness factor of 1.74 has been found for silver foil which has been oxidized in the ammoniacal electrolyte. This roughness factor will be used as a correction for all current density and overpotential data.

Preliminary investigation of alternative methods for the determination of the effective electrolytic surface area of sintered and foil silver electrodes have been performed. The basis for these determinations of the surface area is an oxidation of the silver electrode at a constant potential. The development of the necessary instrumentation for further study is now under way.

Silver foil was oxidized with and without ultrasonic vibrations at various current densities with the temperature controlled to $\pm 0.1^{\circ}C$. The increase in charging capacity was larger at high and low current densities than at moderate current densities. Vibration prior to oxidation failed to increase charging capacity, indicating that no persisting strains in the silver occur and that surface cleaning by the ultrasonic vibrator plays no significant role.

S E C T I O N   I

POTENTIAL AND CURRENT VARIATIONS

OVER THE ELECTRODE SURFACE

Introduction

One of the problems discussed in the Second Quarterly Report[1] of JPL Contract 951911 was the change in the silver electrode surface caused by oxidation in the ammoniacal electrolyte. Electrodes which have been oxidized appear to have a greater surface roughness but the quantitative change in the roughness factor (actual surface area/geometric surface area) was not known. The relationship between the roughness factor and the magnitude of the oxidizing current was also unknown. Because the silver-ammonia electrode is used in our potential and current distribution experiments as well as in the polarization measurements, it is important to determine these changes. The purpose of the experiments reported here is the determination of the physical changes in the electrode surface when it is subjected to extensive oxidation at various current densities in an ammoniacal medium.

Experimental

The modified Haring cell and Luggin capillary system have been described.[2,3] The temperature of all experiments was $20.0 \pm 0.1^{\circ}C$.

The ammoniacal electrolyte has the following composition: $14.7 \underline{F} \ NH_4OH$, $0.10 \underline{F} \ KNO_3$, $0.025 \underline{F} \ AgNO_3$. For the surface area estimations the $0.10 \underline{F} \ KOH$ electrolyte was used. Nessler's reagent $(0.050 \underline{F} \ K_2HgI_4)$ was used to detect ammonia contamination in the $0.10 \underline{F} \ KOH$ electrolyte during roughness factor determinations. All materials used were reagent grade.

Electrode Roughness Factor Experiments

Our objective was the oxidation of the silver electrode in the Haring cell at several current densities in the ammoniacal electrolyte and the measurement of the changes in roughness factor at these several current densities.

The method used in measuring the effective electrolytic surface area was the one described in previous reports.[2] In this method the depth of oxidation (Ag to Ag_2O) on a precisely flat silver surface is assumed to be the same as that for an irregular silver surface if the _actual_ current densities of both surfaces are equal. The current densities are considered equal when the times for the oxidation of the electrodes from silver to silver (I) oxide are experimentally set equal. For the irregular surface, the ratio of current to current density is the surface area.

One difficulty encountered initially was the interference of absorbed ammonia released from the acrylic plastic (Plexiglas) of the Haring cell during the surface area determination. This ammonia passing into the 0.10 $\underline{F}$ KOH electrolyte increased the time of oxidation because of the enhanced solubility of the silver oxide. Additional evidence of the presence of ammonia was obtained by the use of Nessler's reagent which is sensitive to 0.001 mg. NH_3/ml. Continual flushing of the cell with hot water for two or three hours eliminated any detectable trace of ammonia from the cell.

The results of the surface area measurements are presented in Table 1. There was no significant difference in the roughness factors ultimately produced by current densities of 0.127, 1.5, and 6.4 ma/cm^2. For this reason a current density of 6.4 ma/cm^2 was used in most runs made to determine how long it takes for the electrode to reach a constant roughness factor. For this determination electrodes which had been etched with 5 $\underline{F}$ HNO_3 prior to use were compared with electrodes which had been subjected to the usual cleaning procedures. Thus we started with electrodes which had a high roughness factor (HNO_3 etched) and those with a low roughness

factor (cleaned with cleanser). In each case oxidation in ammoniacal electrolyte for 1.5 hour or longer produced a roughness factor of 1.74 $\pm$ 0.03. However, oxidation for a shorter period of time produced lower roughness factors for foil electrodes cleaned with cleanser as in runs 3 and 6 and higher roughness factors for electrodes previously etched in HNO_3 as in runs 7 and 9. Thus a roughness factor of 1.74 will be used to correct all current densities and overpotential data for the range of apparent current densities of 0.13-6.4 ma/cm^2.

Conclusions and Future Work

A roughness factor of 1.74 $\pm$ 0.03 has been found for electrodes which have been oxidized in the ammoniacal electrolyte at currents of 0.13-6.4 ma/cm^2. It takes about 1.5 hour of oxidation at 6.4 ma/cm^2 to reach this roughness factor which remains constant with further oxidation.

We are continuing with experiments which will show how our experimental data compare with theory proposed by Wagner[4] on current density distribution as indicated in the Second Quarterly Report[1] of JPL contract 951911.

S E C T I O N   II

DETERMINATION OF EFFECTIVE ELECTROLYTIC SURFACE AREA

Introduction

The development of methods for the determination of the effective electrolytic surface area of sintered and foil silver electrodes is the objective of this phase of our program. We have developed one method[2] and have checked this method by preparing electrodes of silver spheres of known diameters, calculating surface areas of these electrodes, and then determining the surface areas experimentally for comparison with the calculated values.[3]

Currently we are considering two modifications for determining surface area electrolytically. Some preliminary experiments have demonstrated the need of a precision potentiostat and a current integrator for these studies. The apparatus for these studies is being assembled. In this report we will only outline the rationale of these modifications.

Modification I

In this method the oxidation of the electrode will be effected at a constant potential rather than at constant current. We expect the current to rise rapidly to a peak and then decrease as the thickness of the oxide layer increases, the electrode becoming effectively passivated by the oxide layer. The current flow will be followed on a recorder via an integrating circuit, thereby providing a direct reading of the total charge.

Allen[5] has shown that the thickness of an oxide layer (X) may be determined from the total charge ($q = it$) and the surface area (a). His measurements were made at constant current (i).

$$X = \frac{M\,i\,t}{2F\rho\,a} = k\frac{q}{a}$$

M = molecular weight of oxide, F = faraday, ρ = density of oxide

Our suggestion is that the depth of oxidation at constant potential is

$$X = k\frac{\int i\,dt}{a}$$

and may be the same for smooth and irregular electrodes at that potential. Therefore, we plan to use a potential slightly higher than that needed to oxidize silver to silver(I) oxide but lower than that needed to oxidize silver(I) oxide to silver(II) oxide. A precisely smooth electrode whose surface area is equal to its geometrical area will be used to determine the standard depth of oxidation. Then the charge necessary to passivate an electrode of irregular surface may be used for determination of the actual area of the surface according to the equation

$$X(\text{standard}) = k\frac{q\ (\text{standard})}{a\ (\text{standard})} = X(\text{irregular}) = k\frac{q\ (\text{irregular})}{a\ (\text{irregular})}$$

Modification II

Another approach is based upon the height of the initial peak in the graph of current versus time at constant potential for the oxidation of a silver electrode. This current maximum is a function of potential, surface area of the electrode, and other reaction variables. We suggest that if these other variables are held constant the functional relationship between current maxima and applied potential for precisely smooth surfaces of known area may provide another method for surface area estimation. A graph of current density versus applied potential can be prepared for the smooth electrodes. The current maximum for an electrode of irregular surface can be determined. Then, based on the assumption that the current density maxima are the same for smooth and irregular surfaces at the same potential, a calculation of surface area can be made.

$$A\ (\text{irregular}) = \frac{i\ \text{max (irregular)}}{c.d.\ \text{max (standard)}}$$

Future Work

During the next quarter the experimental data necessary to support or reject these proposals will be acquired.

S E C T I O N   III

THE EFFECTS OF ULTRASONIC VIBRATIONS
ON THE OXIDATION OF SILVER

Introduction

The effects of ultrasonic vibrations on the charging capacity of silver can be studied by observing the change in plateau length of the first oxidation of silver to silver(I) oxide.

It has been demonstrated that an increase of plateau length occurs if the oxidation takes place in an ultrasonic vibrator.[1] The magnitude and cause of this increase as a function of current density have not been adequately studied by earlier experiments.

Skalozubov, Kukoz, and Mikhailenko[6] reported experiments on the effects of ultrasonic vibrations on silver oxidation. They believe that this increase is caused by an increase in surface area. An increase in depth of oxidation could also cause this increase.

An increase in effective surface area or depth of oxidation could be caused by (1) the cleaning action of the vibrations; (2) fracturing of the surface, especially of the oxide layer during oxidation; (3) circulation of electrolyte to previously unreacted surfaces; or (4) other factors not yet considered.

Experimental

The charging capacity is temperature dependent so the temperature of the bath is controlled to $\pm 0.1^{\circ}C$. The thermocouples which were previously used were not sensitive enough and thermometers cannot be used in ultrasonic baths so thermisters were used to determine the temperature to a precision of $\pm 0.01^{\circ}$.

Water from an external bath, controlled at 18.9°C if the vibrator was on or 20.0°C if the vibrator was off, maintained a cell temperature of 20.0 ± 0.1°C. All data were collected at this temperature.

The silver foil electrodes were cleaned with an abrasive cleanser and rinsed thoroughly with distilled water.

Foil electrodes were oxidized both with and without ultrasonic vibrations at each current density and the results were compared. Silver foil was used to prevent any effects due to electrolyte circulation.

Data and Results

Silver foil discs of 0.688 cm^2 geometric area were oxidized at 75, 100, 125, 150, 200, 250, and 300 μamps (109, 145, 182, 218, 291, 363, and 436 μamps/cm^2) with and without vibrations of 80,000 Hz and 80 watts. The charging capacity increased from 10 to 35% at these current densities. The large increases occurred when the oxidation was either rapid (a plateau length of about 1.5 minutes) or slow (a plateau length of about 10 minutes). Reproducibility was better than 4% except for the high current densities which were within 10%. See Table II.

Silver foil discs which were subjected to ultrasonic vibrations for 10 minutes just prior to, but not during, oxidation showed no increase in charging capacity. The plateau length of silver which had never been subjected to vibrations was 2.99 ± 0.02 minutes while the plateau length of the electrodes which were vibrated prior to oxidation was 2.94 ± 0.14 minutes. The difference is well within experimental error limits. See Table III.

Conclusions

The current densities studied were those which are in the range where roughness factor determinations can be made.[2] We suggested in the last report[1] that the long plateaus at low current densities gave more time for fracturing of the oxide to occur,

resulting in larger increases in charging capacity than at high current densities. However, we have found no such relationship between charging capacity increase and current density.

Although the present cleaning method might insert a degree of uncertainty as to how much the surface was roughened during cleaning (producing a non reproducible increase in surface area), there appears to be a definite decrease in the effects of the vibrations from 100 to 300 μamps/cm^2 and an increase from 300 to 450 μamps/cm^2.

Since an increase is noted with foil electrodes, electrolyte circulation is not a factor. The lack of any increase when the electrodes were vibrated in 0.1 N KOH prior to oxidation proves that surface cleaning by the action of the ultrasonic vibrations is not responsible for the increase noted when vibrations are applied during oxidation.

The unstable potential during the last stages of oxidation which was reported previously[1] was found to be due to inadequate electrical contact with the electrode as the oxide layer became thicker. Additional pressure of the platinum holder against the electrode has eliminated this instability.

Future Work

The effects of current density on the increase of charging capacity by vibrations will be further studied to determine how the per cent increase varies at current densities beyond the range already studied.

An electrode cleaning method which will give reproducible surface areas will be sought. After this problem is eliminated a more exact study of the relationship of current density to increase in charging capacity can be made.

A determination for silver ion in the acidified electrolyte after oxidizing the silver will reveal whether a significant amount of oxide has been washed away by the vibrations during oxidation. A comparison of the amount of silver in the electrolyte after oxidation with the increase in plateau length will give a quantitative

estimate of how great a role the loss of oxide from the electrode plays in the increase of charging capacity by ultrasonic vibrations.

TABLE I

Electrode Roughness Factor Experiments

Run No.	Current Density ma/cm^2	Oxidation Time (hr)	Roughness Factor $\frac{(actual\ area)}{(geometric\ area)}$	Electrode History (prior to run)
1	0.127	12	1.75	oxidized at 6.4 ma/cm^2 for 2 hours
2	1.60	1	1.73	oxidized at 6.4 ma/cm^2 for 11 min. and at 0.127 ma/cm^2 for 12 hr. (run no. 1)
3	6.40	.3	1.62	new electrode cleaned with cleanser
4	6.40	.4	1.80	oxidized at 6.2 ma/cm^2 for .3 hr. (run no. 3)
5	6.40	.5	1.72	oxidized at 6.4 ma/cm^2 for .7 hr. (run no. 4)
6	6.40	.3	1.29	new electrode cleaned with cleanser
7	6.40	.5	2.12	new electrode-etched with 5 $\underline{F}$ HNO_3
8	6.40	.5	1.70	oxidized at 6.4 ma/cm^2 for .5 hr. (run no. 7)
9	6.40	.9	2.08	new electrode-etched with 5 $\underline{F}$ HNO_3
10	6.40	3	1.72	new electrode-etched with 5 $\underline{F}$ HNO_3

TABLE II

The Effect of Current Density on the Increase in Charging Capacity

		Plateau Length (Minutes)			
Current Density	With Vibrations	% Average Deviation	Without Vibrations	% Average Deviation	% Increase
109 amps/cm^2	15.46	3	12.13	4	27.5
145	10.66	2	7.88	3	35.3
182	6.85	2	5.74	3	19.3
218	5.54	2	4.64	2	19.4
291	3.72	4	3.39	4	9.7
363	1.94	3	1.68	5	15.5
436	1.64	2	1.28	7	28.1

TABLE III

The Effect of Prior Vibration on Charging Capacity

	Plateau Length (minutes)	
	Without Prior Vibration	With Prior Vibration
	2.98	2.88
	3.03	2.90
	2.98	3.11
	2.98	2.68
	2.97	2.12
average	2.99	2.94
average deviation	1%	5%

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